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(54) Name of the invention: Alumina-Zirconia-Titania Type Grinding Material

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(54) Alumina-Zirconia-Titania Type Grinding Material

Detailed Description of the Invention

1. Name of the Invention

Alumina-Zirconia-Titania Type Grinding Material

2. Scope of the Claims of the Invention

- (1) Alumina-zirconia-titanium type grinding material that is a material obtained as zirconia and titania are added to alumina and melted, and then rapidly cooled, where then as another melting additive material yttrium oxide or rare earth type mineral ore material containing yttrium oxide are included.
- (2) Alumina-zirconia-titanium type grinding material according to Claim 1 of the claims of the present invention where the added amount of yttrium oxide is in the range from 0.05 weight % to 7 weight %, relative to the total amount of the alumina, zirconia, and titania.
- (3) Alumina-zirconia-titanium type grinding material according to Claim 1 of the claims of the present invention where the added amount of the yttrium oxide containing rare earth type ore material is in the range from 0.05 weight % to 7 weight %, relative to the total amount of the alumina, zirconia, and titania.

3. Detailed Explanation of the Invention

This invention is an invention about the improvement of the grinding (polishing) performance of alumina-zirconia-titania type grinding material.

Usually, the alumina-zirconia-type polishing particles are polishing particles that have been quickly expanded in their use as “snacking” of the steel type materials like specialty or stainless steel materials. Namely, compared to the alumina type polishing particles, they have excellent wear resistance and together with that breakage resistance etc., polishing properties, and the fact that under high pressure conditions, they demonstrate superior polishing strength, is the main factor. According to the invention reported in the description of the Japanese Patent Report Number Showa 48-35594, that has been invented previously by the authors of the present invention, an alumina-zirconia-titania material has been obtained that has a polishing performance that is even further increased and more superior than that.

Namely, it is a material where zirconia is added to alumina and together with that then titanium oxide is added in an amount that is in the range of 5 ~ 30 weight % relative to this zirconia amount, and then melted, and because of the fact that it is then quickly cooled, the phenomenon of the phase transformation back to the original zirconia is suppressed, and because of that the high temperature type tetragonal system crystalline phase remains present in an amount in the range of 25 ~ 30 % at normal temperatures, and due to that, it contributes to the increase in the wear resistance properties, breakage resistance properties, etc., polishing properties performance.

However, recently, there is a trend where the polishing methods have also constantly been changing, and the application of fine materials in the so-called heavy grinding field, and especially among those, the significant development of the technology of the change to the light grinding field within the heavy grinding, and also the use of the polishing materials for polishing relative to titanium alloys, has increased. A grinding material that is appropriate for this field is currently required, however, in this case, the required grinding performance is a performance that is higher than that of the above described alumina-zirconia-titania type grinding material, and especially, it is a material that cannot be a severe type of material, and the current status is that a grinding material with satisfactory grinding properties has not yet been obtained.

Namely, in order to be appropriate for the above-described application, it is necessary to suggest a grinding material where however it is stated it has a relatively high amount of zirconia, for example, a grinding material that is formed from a alumina-zirconia co-crystalline material of the type where the amount of zirconia is 40 %. However, in this case, even though it is an

alumina-zirconia-titania material obtained through the above-described titania addition, the ratio of the remaining existing high temperature type tetragonal crystal is extremely low, and the result from the addition is poor. Also, there have been the problems that the initial crystalline α - Al_2O_3 , whose crystal size in the mixed crystalline material is a maximum of 20 microns, is separated at a level of 10 ~ 15 %, and because of that, the predetermined co-crystalline mixed material could not be obtained.

Then the goal of the present invention is to suggest an alumina-zirconia-titania type grinding material where in order that this material be good for application especially relative to heavy grinding, and especially to the light grinding, and then also, relative to titanium alloys, the remaining present amount of the tetragonal crystalline material is extraordinarily increased, and also, the coefficient of the separation of the original crystals of the α - Al_2O_3 is reduced, and because of that the grinding performance is significantly increased. And the characteristics of this material are the fact that it is an alumina-zirconia-titania type grinding material, where then as another additive material yttrium oxide or yttrium oxide containing rare earth ore material, is contained, and it is then called an alumina-zirconia-titania-yttria type grinding material.

Namely, as the additive materials, besides titania, yttrium oxide or yttrium oxide containing rare earth ore material are then added and mixed, and melted, and quickly cooled and by that, a grinding material is obtained that achieves well and satisfies the above described goal. And especially, it is a material where the added amount of the yttrium oxide or yttrium oxide containing rare earth ore material is within the range where it exceeds 0.5 weight % and is up to 7 weight % relative to the total amount of the alumina, zirconia, and titania, and where the zirconia tetragonal crystalline material is crystal separated at a remaining ratio that is in the range of 70 ~ 100 %. And not only that but also, within the same range, the ratio of the separation of the initial crystalline α - Al_2O_3 can be suppressed to a level below 5 weight %.

Moreover, even in the case when the added amount is higher than 7 weight % or below 0.05 weight %, the proportion of the remaining zirconia tetragonal crystal material shows a value that is relatively high compared to the previous technology, and also, the ratio of the separated initial α - Al_2O_3 has a trend where it is significantly suppressed. However, in the case where the added amount exceeds 7 weight %, this leads to the separation of

a cubic crystalline phase, which is not preferable from the point of view of the grinding performance. And in the case when the added amount is less than 0.05 weight %, significant results are not obtained and because of that the range where the added amount is higher than 0.05 weight % and it is up to 7 weight %, is most appropriate, and especially, it is most appropriate that the added amount is within the range of 1 ~ 5 weight %.

Moreover, even, relative to a grinding material that contains an alumina-zirconia co-crystalline material with a relatively small amount of zirconia, for example, 25 %, the same way as in the case of the above-described grinding material that is formed from an alumina-zirconia co-crystallized material that contains a relatively large amount of zirconia, the ratio of the remaining tetragonal crystalline phase zirconia is extremely high, and because of that, the volume change, which occurs at the zirconia transition point is small, and also, the remaining present tetragonal crystalline type zirconia maintains sufficiently its inner part energy, and it has been concluded that there is a trend of improvement of the properties, like good breakage resistance properties, etc.

After that, the practical implementation examples according to the present invention will be explained.

Moreover, as the yttrium oxide or yttrium oxide containing rare earth ore material, that are used in the practical implementation examples according to the present invention, the materials with the analyses values shown according to Table 1, were used.

Table 1

第 1 表

	酸化イットリウム (wt%)	酸化イットリウムを含む 稀土類混合物 (wt%)
Y ₂ O ₃	99.9	60
Fe ₂ O ₃	0.0015	0.013
Na ₂ O	0.0015	—
K ₂ O	0.0015	—
SiO ₂	0.001	0.05
La ₂ O ₃	—	<10
CeO ₂	—	<10
Nd ₂ O ₃	—	<10
Yb ₂ O ₃	—	6
Er ₂ O ₃	—	6.5
Sm ₂ O ₃	—	2

Headings in the table:

1. yttrium oxide (weight %), 2. rare earth ore material containing yttrium oxide (weight %).

Table 2:

Material No.	Y ₂ O ₃ added (wt %)	Al ₂ O ₃	ZrO ₂	TiO ₂	Y ₂ O ₃	Fe ₂ O ₃	SiO ₂	Na ₂ O
1	0	56.94	41.61	1.20	—	0.05	0.12	0.08
2	0.05	57.43	41.25	1.09	0.03	0.04	0.13	0.03
3	0.1	57.91	40.75	1.05	1.05	0.05	0.14	0.04
4	0.5	57.65	40.85	1.02	0.27	0.03	0.14	0.04
5	1	57.12	40.88	1.10	0.64	0.06	0.16	0.04
6	2.5	55.92	41.30	1.03	1.52	0.05	0.14	0.04
7	5	55.16	40.45	1.05	3.09	0.04	0.18	0.03
8	10	52.47	40.12	1.11	6.05	0.05	0.17	0.03

Headings in Table 2:

1. Material number, 2. Y₂O₃ added amount (weight %).

Practical Example 1

A compounding calculation was conducted so that the zirconia in the grinding particles became 40 %, and to 50 kg of Bayer method alumina (99.6 % Al₂O₃), 32.6 kg zirconia (96 % ZrO₂), 0.8 kg of titanium oxide (95 % TiO₂) which corresponds to 2.5 in weight % relative to the zirconia, were mixed and combined, and then, yttrium oxide (99.9 % Y₂O₃) was added in an amount of 0.05, 0.1, 0.5, 1, 2.5, 5, 10 weight % relative to the total amount of the above described three types of materials, and this was then melted using an electrical oven at 95 V, 300 kV, and after that, it was quickly solidified, and melt cast materials were obtained for each addition amount.

Moreover, for the sake of a comparison, a melt cast material where the addition amount of the yttrium oxide was 0 weight %, was also cast.

The values obtained from the analysis of this cast materials, are shown according to the presented in table 2.

After that, the obtained cast material was repeatedly crushed by using an impeller breaker and a crusher, and particle sizes of # 24, and # 60, as determined according to the procedures of the JISR-6001, were withdrawn and obtained.

The ratio of the zirconia crystalline phases of the particle material group # 24, determined by X-Ray Diffraction analysis, is shown according to the presented in Table 3.

Table 3:

第 3 表

1	2	3	4
試料番号	正方晶ZrO ₂ (%)	単斜晶ZrO ₂ (%)	立方晶ZrO ₂ (%)
1	30.1	69.9	0
2	32.1	67.9	0
3	70.7	29.3	0
4	87.9	12.1	0
5	100	0	0
6	100	0	0
7	100	0	0
8	85.8	0	14.2

Headings in table 3:

1. Experimental Material number, 2. tetragonal ZrO₂ (%), 3. monoclinal crystal phase ZrO₂ (%), 4. cubic crystal phase ZrO₂ (%).

As it is clear from the results of the X-Ray Diffraction Analysis, if yttrium oxide is added, compared to the alumina-zirconia-titania type grinding particles according to the previous technology where there is no such addition (Experimental material number 1), it is concluded that there is a trend of a significant increase of the tetragonal crystalline phase amount. And especially, it was confirmed that by the addition of an additive amount in the range of 1 ~ 5 weight %, there was a 100 % tetragonal crystal phase

crystal separation. Also, in the case of the addition of 0.05 weight %, there was a corresponding trend of increase of the amount of the separated tetragonal crystal phase, however, there was no significant difference with the previous technology material, and also, if the added amount exceeded 10 weight %, a separation of a cubic crystalline phase was observed.

On the other hand, at the time when the separation of the initial α - Al_2O_3 of for example a material according to the previous technology (Experimental material 1) and material where the added amount of the yttrium oxide was 0.5 weight % (Experimental material 3), with the same # 24 particle size, was observed by using a metal observation microscope, the results that are shown according to the presented in Figure 1 (A), (B) and Figure 2 (A), (B), were obtained. In each case, the magnification was $\times 100$, and Figure 1 (A), (B), represents an enlarged microphotograph of the Experimental material 1, and its model diagram, and Figure 2 (A), (B), represents an enlarged microphotograph of the Experimental material 3, and its model diagram.

Moreover, in both figures, 1 represents the alumina-zirconia co-crystalline material, and 2 - the α - Al_2O_3 initial crystals.

As it is clear from Figure 1 and Figure 2, in the case of the material with the addition of the yttrium oxide, the separation of the initial α - Al_2O_3 crystals was significantly suppressed, and it was confirmed that the predetermined co-crystalline mixed material, was obtained.

Moreover, it was confirmed that the same trend exists in the case of the other materials where yttrium oxide has been added, however, in the case when the added amount was 0.05 weight %, the separated α - Al_2O_3 was at a level of 10 %, and because of the fact that the material according to the previous technology had a level in the range of 10 ~ 15 %, this trend was almost negligible.

After that, grinding performance tests were conducted relative to the materials with the particle size of # 60.

Namely, a polishing belt was prepared and a polishing test was conducted and the results from that test are shown according to the presented in Table 4.

Moreover, the polishing test was conducted as the size of the belt used was 100 x 2500 m/m, and as the material subject to the polishing SUS-304 was used, and the belt speed was set at 150 m/minute, and the pressure was at 5 kg, and a 10 minute polishing was conducted. Table 4 is a table that shows the comparison of the cumulative mass polished amounts that were obtained by this polishing.

Also, the number in the parentheses shows the comparative value when the case of the material obtained according to the previous technology (Experimental material 1) is set as 100.

Table 4:

第 4 表

1 試料番号	2 累積研磨量 (g)
1	94.4 (Ratio 100)
2	95.0 (" 100)
3	113.0 (" 120)
4	115.7 (" 123)
5	119.2 (" 126)
6	120.6 (" 128)
7	120.4 (" 127)
8	96.0 (" 101)

Headings in the table:

1. Experimental material number, 2. cumulative mass polished amount (g).

Also, the curve line (a) in Figure 3 represents a graph where the cumulative mass polished amounts presented in Table 4, have been plotted.

As it is clear from the above described Table 4 and Figure 3, it has been confirmed that in the case of the co-crystalline grinding particles where yttrium oxide has been added, an extremely excellent polishing strength has been demonstrated compared to the material according to the previous technology where yttrium oxide has not been added.

In this connection, these results are results that correspond to the ratios of the zirconia tetragonal crystalline lattice crystal material, and in the case of the material where the addition amount was 0.05 weight %, there was no significant difference with the material according to the previous technology; and also, in the case when the added amount exceeded 10

weight %, a trend down from the material according to the previous technology was observed due the accompanying separation of cubic crystalline phase material.

However, the addition of the yttrium oxide significantly increases the polishing strength as a total, and not only that, but also, when it is considered that this test results represent only a comparison at the time when a 10 minute polishing has been completed, it is clear that a material is obtained which during the use in practice contributes to the improvement and to achieving extremely excellent polishing performance.

Practical Example 2

A compounding calculation was conducted so that the zirconia in the grinding particles became 40 %, and to 50 kg of Bayer method alumina (99.6 % Al_2O_3), 32.6 kg zirconia (96 % ZrO_2), 0.8 kg of titanium oxide (95 % TiO_2) which corresponds to 2.5 in weight % relative to the zirconia, were mixed and combined, and then, three types of yttrium oxide containing rare earth mineral ore (the materials with analyses values shown according to the presented in Table 1) was added in an amount of 1, 2.5, 5 weight % relative to the total amount of the above described three types of materials (zirconia, alumina, titania), and this material was then melted using an electrical oven at 95 V, 300 kV, and after that, it was quickly solidified, and melt cast materials were obtained for each addition amount.

The values obtained from the analysis of this cast materials, are shown according to the presented in table 5. Moreover, the experimental material number 1 is the same as that in the case of the Practical Example 1 and it is a material according to the previous technology where yttrium oxide has not been added.

Table 5:

表 5 続

試料 番号	Y_2O_3 含有率 (wt%)	Al_2O_3	ZrO_2	TiO_2	合計	Fe_2O_3	SiO_2	Na_2O
1	0	56.94	41.61	1.20	—	0.05	0.12	0.03
9	1	57.35	40.97	1.04	0.42	0.05	0.13	0.03
10	2.5	56.56	41.04	1.09	1.05	0.06	0.16	0.04
11	5	56.19	40.33	1.12	2.11	0.05	0.17	0.03

Headings in Table 5:

1. Experimental material Number, 2. Added amount of yttrium oxide containing rare earth mineral ore (weight %).

*Rare earth type other than Y₂O₃.

After that, the obtained cast material was repeatedly crushed by using an impeller breaker and a crusher, and particle sizes of # 24, and # 60, as determined according to the procedures of the JISR-6001, were withdrawn and obtained.

The ratio of the zirconia crystalline phases of the particle material group # 24, determined by X-Ray Diffraction analysis, is shown according to the presented in Table 6.

Table 6:

1 2 3 4

材料番号	正方晶ZrO ₂ (%)	単斜晶ZrO ₂ (%)	立方晶ZrO ₂ (%)
1	30.1	69.9	0
9	96.4	3.6	0
10	100.0	0	0
11	100.0	0	0

Headings in table 6:

1. Experimental Material number, 2. tetragonal ZrO₂ (%), 3. monoclinal crystal phase ZrO₂ (%), 4. cubic crystal phase ZrO₂ (%).

As it is clear from the results of the X-Ray Diffraction Analysis, if yttrium oxide containing rare earth mineral ore is added, the same way as in the case of the addition of yttrium oxide, compared to the alumina-zirconia-titania type grinding particles according to the previous technology where there is no such addition (Experimental material number 1), it is concluded that there is a trend of a significant increase of the tetragonal crystalline phase amount.

And it was confirmed that by the addition of an additive amount in the range of 2.5 ~ 5 weight %, there was a 100 % tetragonal crystal phase crystal separation.

After that, grinding performance tests were conducted relative to the materials with the particle size of # 60.

The experimental conditions are the same as those in the case of the Practical Example 1 and the results from that test are shown according to the presented in Table 7.

Table 7:

第 7 表

試料番号	磨粒研削量 (g)
1	94.4 (Ratio 100)
9	118.7 (" 126)
10	120.0 (" 127)
11	119.2 (" 126)

Headings in the table:

- Experimental material number, 2. cumulative mass polished amount (g).

Also, the curve line (b) in Figure 3 represents a graph where the cumulative mass polished amounts presented in Table 7, have been plotted.

As it is clear from the above described Table 7 or Figure 3, it has been confirmed that in the case of the co-crystalline grinding particles where yttrium oxide containing rare earth mineral ore has been added, the same way as in the case described in the Practical Example 1 where yttrium oxide was added, an extremely excellent polishing strength has been demonstrated for the obtained co-crystalline grinding particles.

Practical Example 3

A compounding calculation was conducted so that the zirconia in the grinding particles became 40 %, and to 50 kg of Bayer method alumina (99.6 % Al_2O_3), and to 32.6 kg zirconia (96 % ZrO_2), 1.7 and 4.9 kg of titanium oxide, which corresponds to 5 and 15 weight % relative to the zirconia, were mixed and combined, and then, yttrium oxide was added in an

amount of 0.5 weight % relative to the total amount of the above described three types of materials. And for this material, the results from the analyses of the cast material, the ratio of the zirconia crystalline lattice types according to the X-Ray Diffraction for the particle size # 24, and the cumulative mass polished amount for the particle size # 60, were measured.

These results are correspondingly shown according to the presented in Table 8, Table 9 and Table 10.

Moreover, for the sake of a comparison, the values in the case when there was no addition of yttrium oxide regarding the material where 2.5 weight % of titanium oxide was added, and the materials with the corresponding titania addition amounts, are also reported.

Also, in each case the testing methods are the same as those reported according to the Practical Example 1 and the Practical Example 2.

Table 8:

試料番号	TiO ₂ 添加量 (%)	Y ₂ O ₃ 添加量 (wt%)	Al ₂ O ₃	ZrO ₂	TiO ₂	Y ₂ O ₃	Fe ₂ O ₃	SiO ₂	Na ₂ O
1	2.5	0	56.94	41.61	1.20	—	0.05	0.12	0.06
4	2.5	0.5	57.65	40.85	1.02	0.27	0.03	0.14	0.04
12	5	0	57.06	40.63	2.06	—	0.03	0.18	0.04
13	5	0.5	56.78	40.71	2.04	0.25	0.04	0.15	0.03
14	15	0	54.16	39.72	5.91	—	0.03	0.14	0.04
15	15	0.5	53.41	40.24	5.83	0.29	0.04	0.15	0.04

Headings in table 8:

1. Experimental material number, 2. TiO₂ added amount (%), 3. Y₂O₃ added amount (%).

Table 9:

試料番号	正方晶 ZrO ₂ (%)	单斜晶 ZrO ₂ (%)
1	30.1	69.9
4	87.0	12.1
12	33.0	67.0
13	90.2	9.8
14	34.2	65.8
15	93.6	6.4

Headings in Table 9:

1. Experimental Material number, 2. tetragonal ZrO₂ (%), 3. monoclinal crystal phase ZrO₂ (%).

Table 10:

第 10 表

試料番号	累積研削量 (g)
1	94.4 (Ratio 100)
4	115.7 (" 123)
12	95.0 (" 100)
13	112.5 (" 119)
14	92.0 (" 97)
15	117.3 (" 124)

Headings in Table 10:

1. Experimental material number, 2. cumulative mass polished amount (g).

As it is clear from the tables, it is shown that together with the increase of the addition amount of the titanium oxide, there is a trend of increase of the ratio of the remaining present tetragonal crystalline phase ZrO₂, however, to that, also, by the addition of the yttrium oxide, a significant increase trend was observed.

Practical Example 4

The materials obtained as compounding calculations were conducted so that the zirconia in the grinding particles became 25 % and 32 %, and relative to 50 kg and together with that 24.5 kg of Bayer method alumina (99.6 % Al₂O₃), and 16.6 kg and together with that 11.5 kg of zirconia (96 % ZrO₂), correspondingly as weight percent, 0, 2.5, 5, 10, 15, 20, 30 and 40 % of titanium oxide (95 % TiO₂) were added, and the materials where compounding calculations were conducted so that the zirconia in the grinding particles became 25 %, and where relative to 50 kg of Bayer method alumina (99.6 % Al₂O₃); and 16.6 kg of zirconia (96 % ZrO₂), correspondingly as weight percent, 0, 5, 10, 15, 20, 30 and 40 % of titanium oxide (95 % TiO₂) were added, and then yttrium oxide was correspondingly added in an amount of 0.5 weight % relative to the total amount of the above described three types of materials, were correspondingly then melted by an arc heat using an electrical oven, and after that, it was quickly solidified, and these materials were then made into particles by following the usual grinding

particle manufacturing methods, and they were made into JIS #12 grinding particles.

These materials, namely, relative to the types without the yttrium oxide addition, which contain 25 % zirconia and 32 % zirconia, and the type where yttrium oxides has been added and which contains 25 % zirconia, the break resistance measurement test was conducted. For the break resistance measurement test the single particle break strength was used. In this method, the experimental material is granulized to a particle size in the range of 1680 ~ 2000 microns, and by the shrinkage method it is made into a small experimental material, and from within that sample, randomly, 100 units are taken out, and these are measured for their pressure resistance strength one by one, by using a 2 ton amsura compressing equipment. The average value of these measurements was used as the value for the single particle break pressure strength.

The single particle break pressure strength of these grinding particles is shown according to the presented in Table 11 and the relationship between the single particle break pressure strength and the TiO_2/ZrO_2 ratio, is presented in Figure 4.

Table 11:

第 11 表

試料番号	タイプ	TiO_2/ZrO_2 (%)							
		0	2.5	5	10	15	20	30	40
10	Y ₂ O ₃ 無添加 ZrO ₂ 25% タイプ 3	46.0	48.8	51.8	61.0	60.0	58.9	52.2	46.7
17	Y ₂ O ₃ 無添加 ZrO ₂ 32% タイプ 4	46.3	47.5	52.8	62.0	63.3	62.0	49.3	46.0
18	Y ₂ O ₃ 無添加 ZrO ₂ 25% タイプ 5	48.1	—	55.8	64.7	64.2	63.3	54.1	48.0

Headings in Table 11:

1. Experimental material number, 2. type, 3. type without addition of Y₂O₃, and 25 % ZrO₂, 4. type without addition of Y₂O₃ and with 32 % ZrO₂, 5. type with the addition of Y₂O₃ and with 25 % ZrO₂.

As it is clear from the presented in Figure 4, in the case of any of these types of materials, when the ratio $\text{TiO}_2/\text{ZrO}_2$, expressed as weight %, is within the range of 10 ~ 20 %, the strength shows a maximum value, and when the ratio becomes 40 %, there is a decrease. And especially, in the case of the material where yttrium oxide has been added, it was confirmed, naturally, that the type of material where the amount of the ZrO_2 was 25 % is a material which demonstrates an especially excellent break resistance performance compared that in the case when 32 % of zirconia has been added.

As described here above, in the case of the present invention, it is an invention about an alumina-zirconia-titania type grinding material, that is formed as to alumina, zirconia and titania are added and melted, and then quickly cooled, and then, as another melt additive material, yttrium oxide or yttrium oxide containing rare earth mineral ore is contained, and by that, it becomes a material where the maximum remaining zirconia tetragonal crystalline phase is 100 %, and also, even though it is a grinding material that is formed from an alumina-zirconia co-crystalline material with a relatively high amount of zirconia, the amount of the separated (precipitated) initial crystals of the $\alpha\text{-Al}_2\text{O}_3$ is suppressed to less than 5 %, and because of that it is possible to suggest a material which has a significantly improved grinding performance.

Consequently, it is a material that can be used appropriately in heavy grinding also, and especially, in its light grinding field, and also then, it can be appropriately used relative to titanium alloys.

Also, even though it is an alumina-zirconia type grinding material that contains a relatively small amount of zirconia, compared to the materials according to the previous technology, it is a material whose break resistance strength etc., properties are further improved.

4. Brief Explanation of the Figures

Figure 1 (A), (B), represent the enlarged microphotograph and the model type diagram of the obtained according to the previous technology alumina-zirconia co-crystalline mixed material, which has no added yttrium oxide (Experimental material number 1).

Figure 2 (A), (B), represent the enlarged microphotograph and the model type diagram of the obtained according to one practical example of the present invention alumina-zirconia co-crystalline mixed material, which has added yttrium oxide (Experimental material number 3).

Figure 3 is a diagram showing the relationship between the added amount of yttrium oxide etc., which is found in the grinding material with added yttrium oxide and added yttrium oxide containing rare earth mineral ore, according to the same practical example and another practical example, and the cumulative mass polished amount.

Figure 4 is a diagram showing the relationship between the added amount of the titanium oxide found in the grinding material with relatively low zirconia amount and the single particle pressure break strength.

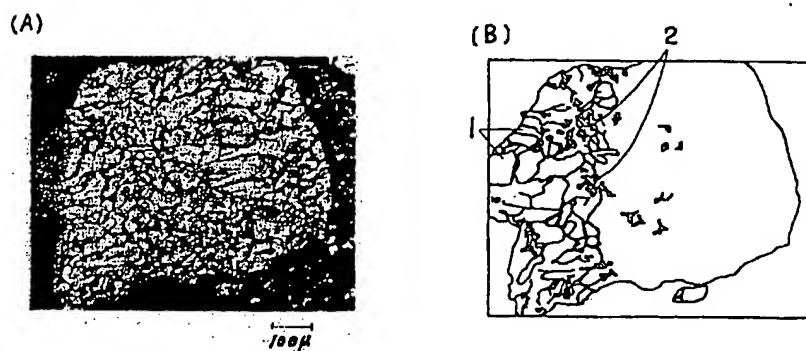


Figure 1: (A) and (B)

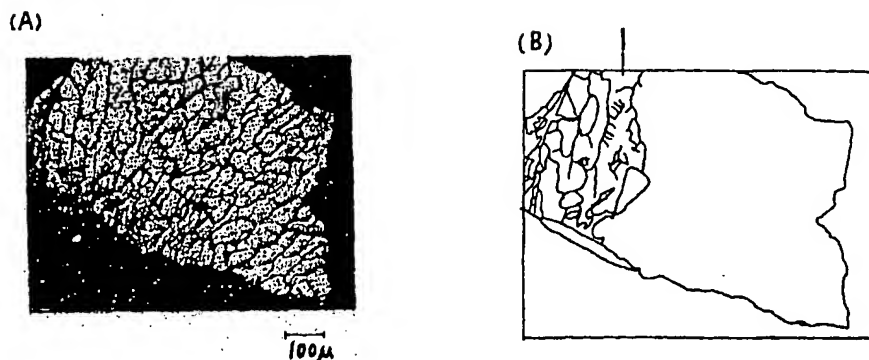


Figure 2: (A) and (B)

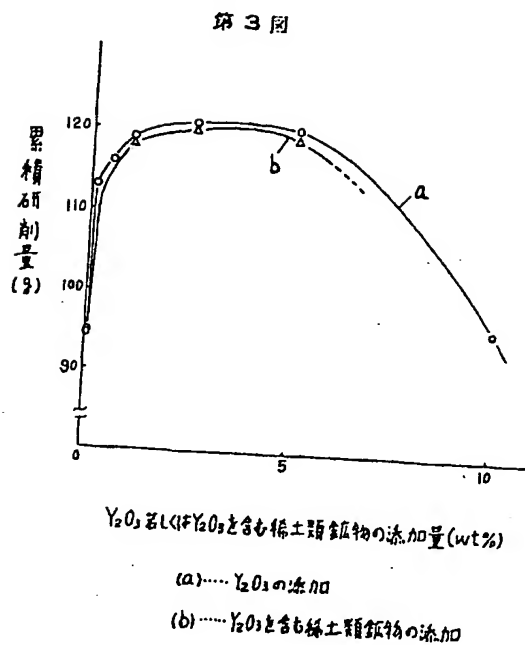


Figure 3:

On the vertical axis – cumulative mass polished amount (g)
On the horizontal axis – added amount of Y₂O₃ or Y₂O₃ containing rare earth mineral ore (weight %)

- (a)..... Y₂O₃ added amount
(b)..... Y₂O₃ containing rare earth mineral ore added amount

第4図

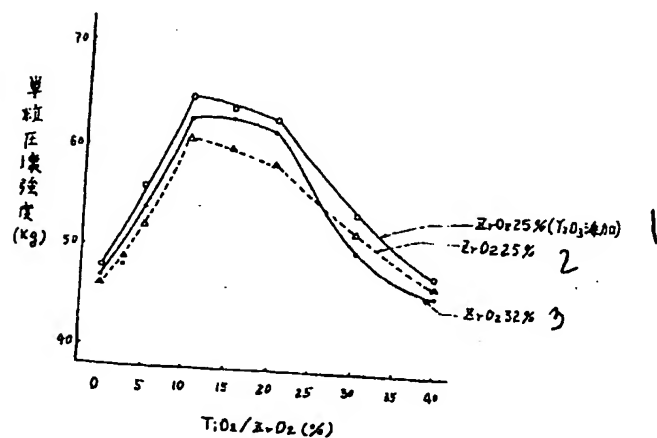


Figure 4:

On the vertical axis – single particle pressure break strength (kg)

On the horizontal axis – TiO₂/ZrO₂ (%)

1. ZrO₂ – 25 % (no Y₂O₃ added)
2. ZrO₂ – 25 %
3. ZrO₂ – 32 %

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⑭ アルミナ—ジルコニア—チタニア系研削材

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明 細 書

1. 発明の名称

アルミナ—ジルコニア—チタニア系
研削材

2. 特許請求の範囲

(1) アルミナにジルコニア及びチタニアを添加溶解し、急冷してなるアルミナ—ジルコニア—チタニア系研削材において、さらに他の溶解添加物として酸化イットリウム又は酸化イットリウムを含む稀土類化合物を含有するアルミナ—ジルコニア—チタニア系研削材。

(2) 酸化イットリウムの添加量が、アルミナ、ジルコニア、及びチタニアの全量に対し0.05wt%を超え7wt%に至る特許請求の範囲第1項記載のアルミナ—ジルコニア—チタニア系研削材。

(3) 酸化イットリウムを含む稀土類化合物の添加量が、アルミナ、ジルコニア及びチタニアの全量に対し0.05wt%を超え7wt%に至る特許請求の範囲第1項記載のアルミナ—ジルコニア—チタニア系研削材。

ア系研削材。

3. 発明の詳細な説明

この発明はアルミナ—ジルコニア—チタニア系研削材における研削性能の改良に関するものである。

一般にアルミナ—ジルコニア系砥粒は、ここ数年間において特殊鋼やステンレス鋼等の鉄鋼材料のスナッキング用として急速に伸びてきた砥粒である。すなわちアルミナ系砥粒に比して耐摩耗性並びに抗破砕性等の研削性能に優れ、高圧下において優秀な研削力を発揮することがその主因であるが、本発明者が先に開示した 特公昭48—35594号公報所載の発明では、それにも増してさらに一層すぐれた研削性能を具備するアルミナ—ジルコニア—チタニア系研削材を提供し得たものであった。

すなわち、アルミナにジルコニアを加えるとともに、そのジルコニア量に対し5～30wt%の酸化チタンをさらに添加して溶解し、急冷するというもので、ジルコニア本来の転移現象に着目し、

高温型正方晶結晶を常温において25~30%程度残存させ、もって耐摩耗性、抗破砕性等の研削性能の向上に寄与せしめたものであった。

ところで近時では研削方法も次第に変化する傾向にあって、重研削という分野においても細分化され、その中でも特に重研削の中の軽研削分野への転換が技術の進歩に従い顕著になりつつある外、チタン合金に対する研削といった研削材上新分野への応用も増大しつつある。このような中においてこれらの分野に対し良好に適応する研削材が今日とみに要求されるところであるが、この場合、要求される研削性能は前記アルミナ-ジルコニア系研削材にも増して更にシビアなものとならざるを得ないものがあり、未だ満足できる研削材を得るに至っていないのが現状である。

すなわち上記のごとき用途に適應させるためには、どちらかといえばジルコニア量を比較的多量とした例えばジルコニア量40%タイプのアルミナ-ジルコニア共晶体からなる研削材を提供する必要があるが、この場合では、前述のチタニア添

加によるアルミナ-ジルコニア-チタニア系研削材であっても高温型正方晶結晶の残存率は未だ極めて低く、添加効果は乏しいものであり、また結晶混合物中に結晶の大きさが $\max 20\mu$ もある初晶の $\alpha\text{-Al}_2\text{O}_3$ が10~15%程度の比率で析出することから、所定の共晶混合物を得られないといった問題点を有していたものである。

そこでこの発明の目的とするところは、重研削の中でも特にその軽研削に対し、またさらにチタン合金に対して格別に良好に適応して使用することができるようになる為、正方晶結晶の残存率を飛躍的に高め、かつ初晶の $\alpha\text{-Al}_2\text{O}_3$ の析出率を減少させ、もって研削性能が一層と向上したアルミナ-ジルコニア-チタニア系研削材を提供しようとするところにあり、その特徴とするところは、アルミナ-ジルコニア-チタニア系研削材において、さらに他の添加物として酸化イットリウムまたは酸化イットリウムを含む稀土類化合物を含有させた、いわばアルミナ-ジルコニア-チタニア-イットリウム系研削材としたところにある。

すなわち添加物としてチタニアの外、酸化イットリウムまたは酸化イットリウムを含む稀土類化合物をさらに添加混入して溶融し、急冷化することにより上掲目的を十分かつ良好に達成した研削材を得たものであって、特に酸化イットリウムまたは酸化イットリウムを含む稀土類化合物の添加量が、アルミナ、ジルコニア及びチタニアの全量に対し0.05wt%を超え7wt%に至る範囲内においては、ジルコニアの正方晶結晶を70~100%の残存率で抽出させることができたものであり、しかも同範囲内においては初晶の $\alpha\text{-Al}_2\text{O}_3$ の析出率を5wt%以下に抑えることができたものである。

なお無論7wt%以上もしくは0.05wt%以下の添加量であってもジルコニア正方晶結晶の残存率は従来に比して比較的大きな値を示し、かつ初晶の $\alpha\text{-Al}_2\text{O}_3$ の析出率を若干抑制する傾向はあるが、7wt%以上の添加では研削性能の向上の点から好ましくない立方結晶の析出につながり、0.05wt%以下では乏しい効果は現われないこ

とから、0.05wt%を超え7wt%に至る範囲内が適切で、特に1~5wt%の範囲内が最も好ましい。

なおまた、比較的小量のジルコニア量、例えば25%タイプのアルミナ-ジルコニア共晶体を含む研削材に対しても、上述の比較的多量のジルコニア量のアルミナ-ジルコニア共晶体からなる研削材と同じく、正方晶ジルコニアの残存率が極めて高いことから、ジルコニアの転移点における容積変化が少なく、また残存した正方晶形ジルコニアが内部エネルギーを十分保有するに至り、良好な抗破砕性等の特性の向上が認められたものである。

次に本発明の実施例について説明する。

なお、本発明の実施例において使用する酸化イットリウム並びに酸化イットリウムを含む稀土類化合物は第1表に示した分析値のものを用いた。

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第 1 表

	酸化イットリウム (wt%)	酸化イットリウムを含む 稀土類添加物 (wt%)
Y ₂ O ₃	99.9	60
Fe ₂ O ₃	0.0015	0.013
Na ₂ O	0.0015	—
K ₂ O	0.0015	—
SiO ₂	0.001	0.05
La ₂ O ₃	—	<10
CeO ₂	—	<10
Nd ₂ O ₃	—	<10
Yb ₂ O ₃	—	6
Er ₂ O ₃	—	6.5
Sa ₂ O ₃	—	2

実施例 1.

砥粒中のジルコニアが40%となるように配合計算を行ない、バイヤー法アルミナ(99.6% Al₂O₃)50 kg、ジルコニア(96% ZrO₂)32.6 kgに、ジルコニアに対し重量パーセントで2.5%に相当する酸化チタン(95% TiO₂)0.8 kgを混合し、さらに酸化イットリウム(99.9% Y₂O₃)を前3種の全量に対し0.05、0.1、0.5、1、2.5、5、10 wt%添加して、溶融炉において95V300 kwで溶融し、しかる後急冷固化して各種添加量についての溶融製造物を得た。

なお比較のために酸化イットリウムの添加量が0 wt%である溶融製造物も同条件で製造した。

これらの製造物の分析値を第2表に示す。

(以下次頁)

第 2 表

試料番号	Y ₂ O ₃ 添加量 (wt%)	Al ₂ O ₃	ZrO ₂	TiO ₂	Y ₂ O ₃	Fe ₂ O ₃	SiO ₂	Na ₂ O
1	0	56.94	41.61	1.20	—	0.05	0.12	0.08
2	0.05	57.43	41.25	1.09	0.03	0.04	0.13	0.03
3	0.1	57.91	40.75	1.05	1.06	0.05	0.14	0.04
4	0.5	57.65	40.85	1.02	0.27	0.03	0.14	0.04
5	1	57.12	40.88	1.10	0.64	0.06	0.16	0.04
6	2.5	55.92	41.30	1.03	1.52	0.05	0.14	0.04
7	5	55.16	40.45	1.05	3.09	0.04	0.18	0.03
8	10	52.47	40.12	1.11	6.05	0.05	0.17	0.03

次にこの得られた製造物をインペラーブレーカー及びロールクラッシャーを用いて繰り返し粉砕を行ない、JIS R-6001に定められた粒度#24、#60で各々採取した。

粒度#24についてX線回折によるジルコニアの結晶形の比率を第3表に示す。

(以下次頁)

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第3表

試料番号	1	2	3	4
	正方晶ZrO ₂ (%)	正方晶ZrO ₂ (%)	正方晶ZrO ₂ (%)	正方晶ZrO ₂ (%)
1	30.1	69.9	0	
2	32.1	67.9	0	
3	70.7	29.3	0	
4	87.9	12.1	0	
5	100	0	0	
6	100	0	0	
7	100	0	0	
8	85.8	0	14.2	

X線回折の結果明らかのように、酸化イットリウムを添加すれば、添加しない従来のアルミナ-ジルコニア-チタニア系結晶（試料番号1）に比し、正方晶の結晶が著しく増大する傾向にあることが認められ、特に1~5wt%の添加量では100%の正方晶結晶が晶出していることが認められた。また添加量が0.05wt%では一応正方晶の晶出の増大傾向はあるものの、従来のものとあまり大差はなく、また10wt%を超えると立方晶の析出が認められた。

一方、この同じ粒度#24のものであって、例えば従来のもの（試料番号1）と酸化イットリウム添加量0.5wt%（試料番号3）のものについて金屈顕微鏡を用いて初晶の α -Al₂O₃の析出状態を観察したところ、第1図（A）（B）及び第2図（A）（B）に示される様な結果が出た。いずれも倍率は $\times 100$ で、第1図（A）（B）は試料番号1のものの拡大写真及びその模式図、第2図（A）（B）は試料番号3のものの拡大写真及びその模式図である。

なお両図において、1はアルミナ-ジルコニア共晶、2は α -Al₂O₃の初晶である。

第1図及び第2図からも明らかなごとく、酸化イットリウムを添加したものの方は著しく α -Al₂O₃の初晶の析出が抑制されており、所定の共晶混合物が得られていることが認められた。なお他の酸化イットリウムの添加のものにあっては同様の傾向があることが確かめられているが、添加量が0.05wt%では α -Al₂O₃の析出は10%程度あり、従来のものが10~15%程度であることからすると幾分その傾向が出ているとはいえるものの、あまり著しい差はなかった。

次に粒度#60について研削性能の試験を行った。

すなわち研摩ベルトを作成し、研削テストを行なったものであり、その結果については第4表に示す。

なお研削テストは、使用するベルトサイズを100 \times 2500 \times ノ、被研削材をSUS-304として、ベルトスピード150 \times ノ、圧

力5kgで、10分間研削を行なったものであり、第4表はその研削によって得られた累積研削量をもって比較したものである。

また括弧内は従来のもの（試料番号1）を100とした場合の比較値を示す。

第4表

試料番号	1	2
	累積研削量 (g)	累積研削量 (g)
1	94.4 (Ratio 100)	
2	95.0 (" 100)	
3	113.0 (" 120)	
4	115.7 (" 123)	
5	119.2 (" 126)	
6	120.6 (" 128)	
7	120.4 (" 127)	
8	96.0 (" 101)	

また第3図における曲線(a)は、この第4表における累積研削量をプロットしたグラフであ

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る。

上記第4表あるいは第3図から明らかなように、酸化イットリウムを添加する共晶結粒は酸化イットリウムを添加しない従来のものに比して極めて優れた研削力を発揮することが認められた。

因みにこの結果は大略第3表に示したジルコニア正方晶結晶の比率に対応しているものであって、添加量0.05wt%のものでは従来のものとあまり大差はなく、10wt%を超えると立方晶の析出に伴い従来のものよりダウンする傾向がみられる。

しかしながら酸化イットリウムの添加は、全体としては研削力の増大傾向を著しくするものであり、しかもこのテスト結果がわずか10分間の研削時間における比較であることを考えたとき、実際の使用にあっては極めて優れた研削性能の向上に寄与し得るものである。

実施例2.

砥粒中のジルコニアが40%となるように配合計算を行ない、バイヤー法アルミナ(99.6% Al_2O_3) 50 kg、ジルコニア(96%

ZrO_2) 32.6 kgに、ジルコニアに対し重量パーセントで2.5%に相当する酸化チタン(95% TiO_2) 0.8 kgを混合し、さらに酸化イットリウムを含む稀土類鉱物(第1表に示す分析値のもの)を前3種の全量に対し1、2.5、5wt%添加して、電気炉において95V、300 kwで溶融し、しかる後急冷固化して各種添加量についての溶融結造物を得た。

これらの結造物の分析値を第5表に示す。なお試料番号1は前記実施例1と同じく酸化イットリウム無添加の従来のものである。

(以下次頁)

第5表

試料番号	Y_2O_3 を含む稀土類鉱物の添加量(wt%)	Al_2O_3	ZrO_2	TiO_2	%	Fe_2O_3	SiO_2	Na_2O
1	0	55.94	41.51	1.20	—	0.05	0.12	0.08
9	1	57.36	40.97	1.04	0.42	0.05	0.13	0.03
10	2.5	56.56	41.04	1.09	1.05	0.06	0.16	0.04
11	5	56.19	40.33	1.12	2.11	0.05	0.17	0.03

% Y_2O_3 その他稀土類

次にこの得られた結造物をインペラーブレーカー及びロールクラッシャーを用いて繰り返し粉碎を行ない、JIS R-6001に定められた粒度#24、#60で各々採取した。

粒度#24についてX線回折によるジルコニアの結晶形の比率を第6表に示す。

(以下次頁)

1 2 3 4

第 6 表

試料番号	正方晶 ZrO ₂ (%)	単斜晶 ZrO ₂ (%)	立方晶 ZrO ₂ (%)
1	30.1	69.9	0
9	96.4	3.6	0
10	100.0	0	0
11	100.0	0	0

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X線回折の結果明らかなように、酸化イットリウムを含む稀土類酸物を添加すれば、酸化イットリウムの添加の場合と同じく、添加しないアルミナ-ジルコニア-チタニア系酸化物（試料番号1）に比し、正方晶の結晶が著しく増大する傾向があることが認められ、2.5~5wt%の添加量では100%の正方晶結晶が晶出していることが認められた。

次に粒度#60について研削性能の試験を行なった。

試験条件は実施例1と同様である。その結果については第7表に示す。

第 7 表

試料番号	累積研削量 (g)
1	94.4 (Ratio 100)
9	118.7 (" 126)
10	120.0 (" 127)
11	119.2 (" 126)

また第3図における曲線(b)はこの第7表における累積研削量をプロットしたグラフである。

上記第7表あるいは第3図から明らかなように、酸化イットリウム添加の実施例1の場合と同様に、酸化イットリウムを含む稀土類酸物を添加する共晶酸化物においても優れた研削力を発現することが認められた。

実施例3.

砥粒中のジルコニアが40%になるように配合計算を行ない、バイヤー法アルミナ50 kg、ジルコニア32.6 kgにジルコニアに対して重量パーセントで5、15wt%の酸化チタン1.7、4.9 kgを混合し、酸化イットリウムを前3種の混合物に対し重量パーセントで0.5wt%添加したものについて結晶物の分析値、粒度#24についてのX線回折によるジルコニア結晶形の比率及び粒度#60についての累積研削量を測定した。

その結果をそれぞれ第8表、第9表及び第10表に示す。

なお比較のため、酸化チタン2.5wt%の添加

量のもの、及びそれぞれのチタニア添加用のものについての酸化イットリウム無添加の場合の値も併記した。

また試験方法はいずれも実施例1及び実施例2と同様である。

(以下次頁)

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第 8 表

試料番号	TiO ₂ 添加量 (%)	Y ₂ O ₃ 添加量 (wt%)	Al ₂ O ₃	ZrO ₂	TiO ₂	Y ₂ O ₃	Fe ₂ O ₃	SiO ₂	Na ₂ O
1	2.5	0	56.94	41.61	1.20	—	0.05	0.12	0.00
4	2.5	0.5	57.65	40.85	1.02	0.27	0.03	0.14	0.04
12	5	0	57.06	40.63	2.06	—	0.03	0.16	0.04
13	5	0.5	56.78	40.71	2.04	0.25	0.04	0.15	0.03
14	15	0	54.16	39.72	5.91	—	0.03	0.14	0.04
15	15	0.5	53.41	40.24	5.83	0.29	0.04	0.15	0.04

第 9 表

試料番号	正方晶 ZrO ₂ (%)	単斜晶 ZrO ₂ (%)
1	30.1	69.9
4	87.9	12.1
12	33.0	67.0
13	90.2	9.8
14	34.2	65.8
15	93.6	6.4

第 10 表

試料番号	累積研削量 (g)
1	94.4 (Ratio 100)
4	115.7 (" 123)
12	95.0 (" 100)
13	112.5 (" 119)
14	92.0 (" 97)
15	117.3 (" 124)

上記表からも明らかなように、酸化チタンの添加量の増加に伴い正方晶 ZrO₂ の残存率は増大傾向を示しているが、それにも増して酸化イットリウムの添加による著しい増大傾向が認められた。またこれに対応して研削力の増大傾向が累積研削量の数値結果から認められる。

実施例 4.

砥粉中のジルコニアが 2.5 % 並びに 3.2 % になるように配合計算を行ない、バイヤー法アルミナ (99.6 % Al₂O₃) 50 kg 並びに 24.5 kg、ジルコニア (96 % ZrO₂) 16.6 kg 並びに 11.5 kg に、ジルコニアに対して、重量パーセントで 0.2、5、10、15、20、30、40 % の酸化チタン (95 % TiO₂) を各々添加したものと、砥粉中のジルコニアが 2.5 % になるように配合計算を行ない、バイヤー法アルミナ (99.6 % Al₂O₃) 50 kg、：ジルコニア (96 % ZrO₂) 16.6 kg に、ジルコニアに対して重量パーセントで 0.5、10、15、20、

30、40 % の酸化チタン (95 % TiO₂) を添加し、さらに酸化イットリウムを前 3 種の物質全量に対して 0.5 wt% 添加したものをそれぞれ、電気炉を用いてアーク熱で溶融・急冷固化し、これを一般的な砥粒の生産方式に従って整粒し、JIS # 12 の砥粒とした。

これらのもの、すなわち酸化イットリウム無添加のジルコニア 2.5 % タイプ及び 3.2 % タイプのものと、酸化イットリウム添加のジルコニア 2.5 % タイプのものについて抗破砕性測定試験を行なった。抗破砕性測定には単粒圧壊強度を用いた。この方法は、試料を 1680 ~ 2000 ミクロンに整粒して、縮分法により小試料とし、その中からランダムに 100 個採取して、これを 2 トンアムスラー圧縮器で 1 個ずつ耐圧強度を測定して、その平均値を単粒圧壊強度とした。

これらの砥粒の単粒圧壊強度を第 11 表に、単粒圧壊強度と TiO₂ / ZrO₂ との関係を第 4 図に示す。

試料番号	タイプ	TiO ₂ / ZrO ₂ (%)								
		0	2.5	5	10	15	20	30	40	
16	Y ₂ O ₃ 無添加 ZrO ₂ 25% タイプ 3	46.0	48.8	51.8	61.0	60.0	58.9	52.2	46.7	
17	Y ₂ O ₃ 無添加 ZrO ₂ 32% タイプ 4	46.3	47.5	53.8	63.0	63.3	62.0	49.3	45.0	
18	Y ₂ O ₃ 無添加 ZrO ₂ 25% タイプ 5	48.1	—	55.8	64.7	64.2	63.3	54.1	48.0	

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第4図より明らかな様に、いずれのタイプにおいてもTiO₂ / ZrO₂ が重量パーセントで10～20%の範囲内で、max値を示し、10%になると低下するが、特に酸化イットリウムを添加したものについては、ZrO₂ 25%タイプにあっては勿論、32%タイプと比較しても更にすぐれた抗酸蝕性を発現することが認められた。

以上のごとくこの発明は、アルミナにジルコニア及びチタニアを添加溶解し、急冷してなるアルミナ-ジルコニア-チタニア系研削材において、さらに他の溶解添加物として酸化イットリウムまたは酸化イットリウムを含む稀土類化合物を含有させることにより、砥粒中にジルコニア正方晶結晶を最大100%残存させたものであり、また比較的ジルコニア量の多いアルミナ-ジルコニア共晶体からなる研削材にあって初品のα-Al₂O₃の析出を5%以下に抑えたもので、研削性能を著しく向上させた研削材を提供し得たものである。従って本発明の中でも特にその軽研削に対し、またさらにチタン合金に対して格別に良好に適用

して使用できるものである。

また比較的ジルコニア量の少ないアルミナ-ジルコニア共晶体を含む研削材にあっては従来と比較すればその抗酸蝕性等の特性において一段と向上し得たものである。

4. 図面の簡単な説明

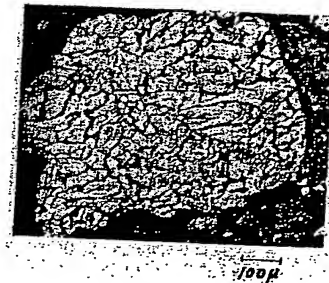
第1図(A)(B)は従来の酸化イットリウム無添加のアルミナ-ジルコニア共晶混合物(試料番号1)の拡大写真及びその模式図、

第2図(A)(B)はこの発明の一実施例である酸化イットリウム添加のアルミナ-ジルコニア共晶混合物(試料番号3)の拡大写真及びその模式図、

第3図は同実施例及び他実施例である酸化イットリウム添加の研削材及び酸化イットリウムを含む稀土類化合物添加の研削材における酸化イットリウム等の添加量と累積研削量の関係図、

第4図はジルコニア量が比較的少ない研削材における酸化チタンの添加量と単位圧強硬度との関係図である。

第 1 図 (A)

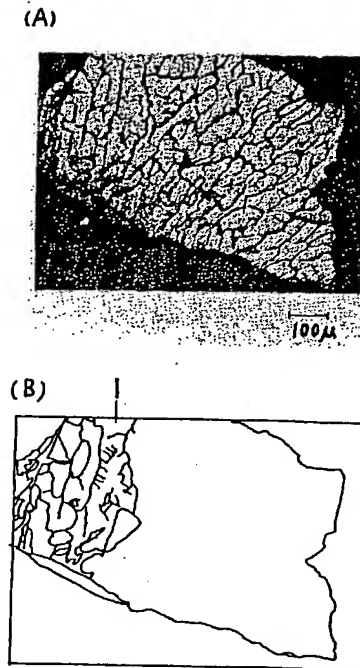


(B)

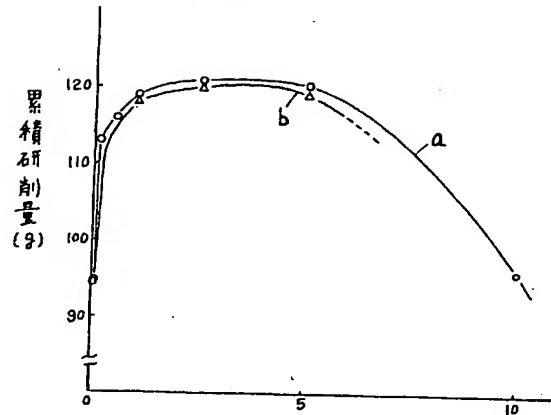


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第2図



第3図

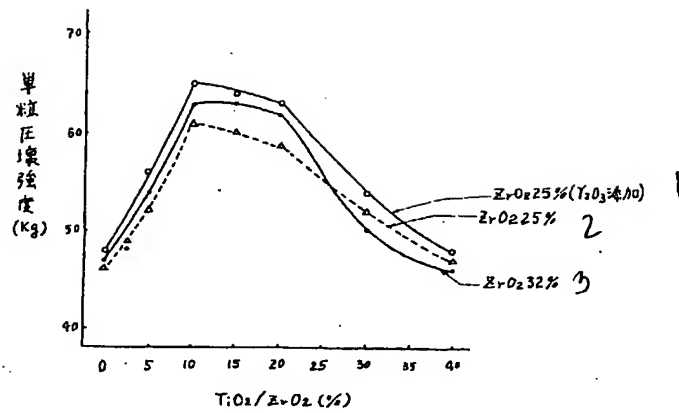


Y_2O_3 若しくは Y_2O_3 を含む希土類酸化物の添加量 (wt%)

(a) Y_2O_3 の添加

(b) Y_2O_3 を含む希土類酸化物の添加

第4図



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